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Infrared spectra of some 2-nitrobenzenesulphenate esters, $2\text{-}NO_2C_6H_4S.O.R$

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Abstract—Infrared spectra of some 2-nitrobenzenesulphenate esters have been obtained; for one of these, $2\text{-}NO_2C_6H_4$—S—O—CH_3, frequency shifts due to ^{18}O substitution in the sulphenate group have been measured. The prominent bands at 990 and 700 cm^{-1} exhibit shifts of 28 and 17 cm^{-1} respectively. Approximate force constant calculations suggest that the modes responsible involve mostly CO and SO stretching respectively. With the methyl esters, a correlation was observed between the frequency of the higher band and the Hammett σ-constants for the 4-substituents.

INTRODUCTION

ALTHOUGH the chemistry of the arylsulphenates Ar—S—O—R has received some attention [1, 2], little information is available on the infrared spectra of this class of compound. The spectra of a series of ethyl 4-substituted-2-nitrobenzenesulphenates have been reported to show strong bands near 1010 and 880 cm^{-1} [1]. These lie fairly close to the bands near 1050 and 800 cm^{-1} respectively in analogous P—O—C compounds, whose assignment has been the subject of some controversy [3–5]. In the S—O—S system [6] a band at 800 cm^{-1} was assigned to the S—O antisymmetric stretching frequency. It was hoped that ^{18}O substitution in the case of methyl 2-nitrobenzenesulphenate would indicate whether or not separate S—O and C—O stretching motions existed in the S—O—C system.

RESULTS

For the methyl compound, infrared spectra were obtained between 1400 and 200 cm^{-1}, partly in CS_2 solution, partly in Nujol mulls, using two different spectrometers, a Hilger H800 instrument with rocksalt or KBr prism and a Perkin–Elmer 225 grating spectrometer. The frequencies found are shown in Table 1.

The main features of the spectrum below 1200 cm^{-1} are the two intense bands at 989 and 700 cm^{-1}, which exhibit ^{18}O shifts of 28 and 17 cm^{-1} respectively.

Data on the intense band near 1000 cm^{-1} in various 4-substituted derivatives in Nujol mulls were recorded on a Perkin–Elmer 237 instrument (see Table 2).

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[1] C. Brown and D. R. Hogg, *J. Chem. Soc. B* 1315 (1968).

[2] S. Braverman and C. Simons, *Ann. Rep. Mechanism Reactions Sulphur Compounds*, Vol. 2, p. 101 (1967); A. Schoberl and A. Wagner, *Methoden der Organischen Chemie* (Edited by E. Müller), Vol. 9, p. 281. G. Thieme (1955).

[3] R. A. Nyquist, *Spectrochim. Acta* **23A,** 1499 (1967).

[4] J. Chatt and B. T. Heaton, *Spectrochim. Acta* **23A,** 2220 (1967).

[5] J. R. Durig and J. S. Di Yorio, *J. Chem. Phys.* **48,** 4154 (1968).

[6] R. J. Gillespie and E. A. Robinson, *Spectrochim. Acta* **19,** 741 (1963).

Table 1. Infrared spectra of methyl 2-nitrobenzenesulphenate and ^{18}O shifts (in brackets)

CS$_2$ solution		Nujol mulls		
1359 vw			592 sp. w	
1336 m			556 m	
1305 sp. s			492·5 sp. vs*	(0)
1274 vw			474 vw	
1259 vw			459 vw	
1244 vw			430·8 s*	(0·5 ± 0·2)
1168 bd. w			420 sp. m	
1152 sp. w			409·8 s*	(4·8 ± 0·2)
1130 bd. vw			376·3 s*	(0)
1101 bd. w		1098 bd. vs	336·5 s*	(2·3 ± 0·5)
1064 w		1061 sp. m	263·5 m*	(8·0 ± 1·0)
1037 w		1037 sp. m	224 w*	(?)
989·5 sp. s*	(28·2 ± 0·2)	987 vbd. vs		
		868 sp. vw		
		846 sp. s		
783 sp. w		783 sp. s		
734 sp. s		734 sp. s		
700·5 sp. s*	(16·8 ± 0·2)	700 bd. vs		
679 bd. w		678 vbd. s		
660 bd. w		659 sp. s		

* P-E spectrometer used here. Elsewhere H800.

Table 2. Frequency (cm^{-1}) of principal band at 1000 cm^{-1} for alkyl 4-substituted-2-nitrobenzenesulphenates (in nujol)

4-substituent	Methyl ester	Ethyl ester	isoPropyl ester	t-Butyl ester
NO$_2$	970	1017	—	—
CF$_3$	975	1018	—	—
CO$_2$H	—	1010	—	—
Cl	985	1020	—	—
H	990	1014	1095	1160
CH$_3$	—	1020	—	—

DISCUSSION

The above isotope shifts on the 989 and 700 cm^{-1} bands in the spectrum of the methyl compound suggest that these may be due to C—O and S—O stretching motions predominating in the respective modes. This was confirmed by approximate force constant calculations.

Assuming an effective mass of 15 for the CH$_3$ group, and ignoring the bending motion, the isotope shifts for the S—O—Me stretching motions were calculated for the complete set of possible force constants, the relevant range of which is reproduced in Table 3, together with the corresponding uncoupled C—O and S—O stretching frequencies which these force constants would imply. The calculated product ratios $\nu_1\nu_2(^{16}O)/\nu_1\nu_2(^{18}O)$ are all higher than the observed ones, presumably due to the neglect of the bending motion. It seems likely however that the C—O and S—O stretching force constants are about 4·2 ± 0·2 and 3·5 ± 0·2 mdyn/Å respectively. The latter value agrees well with the S—O force constant of 3·3 mdyn/Å obtained from Gillespie and Robinson's S—O—S antisymmetric stretching frequency of 800 cm^{-1} [6].

It is not easy to assign the S—O—C bending mode on the basis of our present data. For the in-plane motions of the oxygen atom, the Teller–Redlich product rule predicts an overall frequency ratio of the ^{16}O to the ^{18}O frequencies of about 1·106, after making allowances of 1·011 and 1·007 for the two translations and one rotation in the class. The observed C—O and S—O shifts account for just half of this total (1·055) leaving a residue of 1·049 to be found elsewhere in the spectrum.

Table 3. Force constants and ^{16}O–^{18}O isotope shifts for S—O—CH_3 group

k_{CO}	k_{12}	k_{SO}	$\Delta\nu$ (989)	$\Delta\nu$ (700)	ν_{CO}°	ν_{OS}°
4·35	−0·20	3·36	29·4	22·9	977	731
4·19	−0·01	3·48	30·8	21·9	959	744
4·00	0·15	3·64	32·2	20·9	937	761
3·81	0·27	3·84	33·5	20·0	913	782
observed values			28·2	16·8	989	700

Force constants in mdyn/Å, frequencies in cm^{-1}.

A small contribution would come from the methyl rocking modes near 1150 cm^{-1}. These were unfortunately not studied here, but our previous experience with $CH_3{}^{18}OH$ and $(CH_3)_2{}^{18}O$ spectra [7] makes it unlikely that their contribution would exceed 1·0025.

Almost the whole of the remainder is accounted for if the bands at 410 and 264 cm^{-1} are assigned to the in-plane class, in which case the modes would presumably involve both S—O—C and ring–S bending. It would then be necessary to find another low frequency band or bands for the out-of-plane bending mode, for which the $^{16}O/^{18}O$ ratio would be about 1·05.

This out-of-plane bending mode of course provides an alternative assignment for the band at 264 cm^{-1}: it may well however lie near or below 220 cm^{-1}, which was the practical limit of the 225 spectrometer.

Elsewhere in the spectrum there is a close resemblance to the spectrum of *o*-nitrochlorobenzene. The δ_{NO_2}(sym) and ω_{NO_2} modes can be assigned to bands in the mull at 846 and 556 cm^{-1} respectively.

The intensity pattern near 1300 cm^{-1} however differs from that of the chloro compound and the exact position of ν_{NO_2}(sym) is therefore in doubt.

Turning now to compounds other than methyl 2-nitrobenzenesulphenate, a band is found near 1000 cm^{-1} in all cases, which however increases in frequency with increasing α-substitution in the alkyl group. This band is presumably related to the one found in primary, secondary and tertiary alcohols between 1250 and 1000 cm^{-1} [8] which will contain at least a proportion of C—O stretching. The spectrum of

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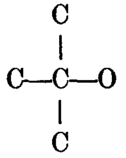
[7] Unpublished work in this laboratory.

[8] H. H. Zeiss and M. Tsutsui, *J. Am. Chem. Soc.* **75**, 897 (1953).

[9] A. R. Philpotts and W. Thain, *Anal. Chem.* **24**, 638 (1952).

the t-butyl ester showed the usual strong band at 845 cm^{-1} characteristic of the



$C-\overset{\overset{C}{|}}{\underset{\underset{C}{|}}{C}}-O$ group [9].

Concerning the band at 880 cm^{-1} in the *ethyl* compounds, ascribed earlier to the S—O—Et system [1], its frequency seems to be too high for an S—O stretching mode and the question of its assignment is therefore left open.

Where the influence of 4-substitution on the frequency of the band near 1000 cm^{-1} was studied (see Table 2), for the case of the *methyl* sulphenates a good correlation was found between the relative frequency shift $(\nu_R - \nu_H)/\nu_H$ and the Hammett σ-constant [10], the plot being linear with $\rho = 0{\cdot}026$ and $r = 0{\cdot}998$. However for the *ethyl* compounds, no such correlation was found.

MATERIALS

The alkyl sulphenates were prepared using known methods [11] from the sulphenyl chloride and the appropriate alcohol. *Methyl 2-nitro-4-trifluoromethylbenzenesulphenate* was obtained as a yellow oil, b.p. 120° at 0·05 mm (Found: S, 12·5, $C_8H_6F_3NO_3S$ requires S, 12·65 %). *t-Butyl 2-nitrobenzenesulphenate* was obtained as yellow crystals from ethanol, m.p. 53·5–54·5° (Found: C, 52·8; H, 6·0; S, 14·0 $C_{10}H_{13}NO_3S$ requires C, 52·8; H, 5·8; S, 14·1 %). Ethyl 4-carboxy-2-nitrobenzenesulphenate was obtained as orange cubic crystals from ethanol, m.p. 147–149°. The m.p.'s of all the other sulphenates were in agreement with the literature values and the NMR spectra were in accord with the expected structures. The ^{18}O labelled methyl 2-nitrobenzenesulphenate was similarly prepared, using ^{18}O-methanol (isotopic purity 95 %) obtained from the YEDA Research and Development Company, and purified by distillation under vacuum.

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[10] H. H. Jaffé, *Chem. Rev.* **53,** 191 (1953).

[11] N. Kharasch, D. P. McQuarrie and C. M. Buess, *J. Am. Chem. Soc.* **75,** 2658 (1953).